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PHOTOLUMINESCENCE IN BERYLLIUM CERAMICS

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The photoluminescence properties of beryllium ceramic obtained by semidry molding with and without deliberately introduced alkali metal impurities are considered. It is assumed that heat treatment of samples in hydrogen and the introduction of lithium and sodium impurities in small quantities lead to the formation of additional luminescent centers increasing the intensity of photoluminescence. In contrast, large concentrations of the impurity phase suppress photoluminescence. In heterovalent replacement of Be^{2+} with Li^+ or Na^+ ions, additional oxygen vacancies are formed, in which electrons can be localized under radiation and F^+ centers can be formed.

Beryllium ceramics is extremely important for dosimetry and can be used in scintillators and working bodies in exothermic-emission and thermoluminescent dosimeters for ionizing radiation [1, 2].

There are numerous publications studying the luminescent properties of single crystals BeO and beryllium ceramics in the course of excitation with various types of radiation: x-ray, gamma-ray, and electrons. With the development of powerful gas lasers radiating in the UV spectrum range, the study of photoluminescence (PL) of beryllium ceramics has become topical.

The production technology of beryllium ceramics and the amount and type of impurities in it have a significant effect on PL in the visible and near-UV spectrum ranges.

The samples were prepared in the shape of disks by semidry molding and sintering in vacuum at the maximum temperature 2223 K to the density 2.84–2.90 g/cm³. Part of the samples with impurities were subjected to additional calcination in hydrogen medium at temperature 1470 K. After sintering, some samples acquired a gray color caused by the presence of impurities. The chemical analysis of the volume and surface of white and tinted samples of beryllium ceramics indicates the presence of iron, silicon, and aluminum impurities.

To determine the effect of impurity ions on the FL output in exciting samples with an excimer pulse laser, ceramic discs were prepared with alkaline metal additives and without specially introduced impurities. Lithium and sodium additives were introduced into porous discs after the first firing by impregnating the disks for a certain time in Li_2CO_3 and NaOH

solutions of various concentrations. The following concentrations of the solutions were prepared (g/liter): 13 Li_2CO_3 , 100, 50, and 10 NaOH . The amount of the impurities persisting in beryllium ceramic samples after the final sintering was not measured.

The luminescence of samples was excited at temperature 300 K with an ArF excimer laser (radiation energy 6.42 eV, pulse power 100–200 kW, duration 5 nsec, repetition frequency 2 Hz, radiation aperture $12 \times 2 \text{ mm}^2$) and with an argon pulse laser with radiation energy 3.67 eV, pulse power 15 kW, and repetition frequency 1 kHz in the temperature range 77–400 K. The luminescence was continuously registered with a MDR-2 monochromator and an FÉU-39A photoelectron multiplier.

The PL spectra of all samplers represent complex curves with wide and strongly overlapping maximums in the range of 3.35–3.48 eV.

The PL spectra of the reference samples, to which no impurities were deliberately introduced, differed from the samples with Li and Na impurities mostly in their luminescence intensity. It was found that the PL maximums in ceramics with impurities (especially after impregnation in NaOH of the concentration 100 g/liter) are shifted toward lower (by 0.14 eV) energy values compared to the reference samples.

The intensity of PL in ceramics was measured with respect to the brightest sample (Li_2CO_3 — 13 g/liter, heat-treated in hydrogen) depending on the concentration of alkali metal solutions, in which the samples were impregnated, and additional heat treatment in hydrogen medium. (Table 1). It was found that the PL intensity of samples treated in hydrogen exceeded 1.1–1.6 times the intensity of the samples not subjected to calcination in hydrogen.

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TABLE 1

Sample	Treatment conditions*	Relative intensity of PL, %	FL maxima, eV
1	Impregnation in Li_2CO_3 (13 g/liter) with subsequent heat treatment in hydrogen	100.0	3.47
2	The same, without treatment in hydrogen	60.0	3.47
3	Impregnation in NaOH (100 g/liter) with subsequent heat treatment in hydrogen	22.8	3.35
4	The same, without treatment in hydrogen	16.6	3.35
5	Impregnation in NaOH (50 g/liter) with subsequent heat treatment in hydrogen	38.4	3.40
6	The same, without treatment in hydrogen	26.0	3.40
7	Impregnation in NaOH (10 g/liter) with subsequent heat treatment in hydrogen	84.0	3.47
8	The same, without treatment in hydrogen	76.0	3.47
9	Reference sample (without introduced impurities)	28.0	3.49

* Excitation by laser with radiation energy 6.42 eV.

As can be seen from Table 1, the maximum PL intensity was registered in ceramic samples impregnated in a solution of 13 g/liter Li_2CO_3 and 10 g/liter NaOH, and the minimum intensity was seen after impregnation in a solution of 100 g/liter NaOH.

A pulse power of the eximer laser equal to 150 – 200 kW makes it possible to excite PL in opaque samples 2.5 – 3.5 mm thick. In thick samples (over 3.5 mm) a substantial loss in the PL output is observed due to intense dissipation and absorption.

The ceramic samples, to which impurities were not added, after sintering in a forevacuum in a carbon charge (with maximum temperature 2223 K), besides the white color, exhibited a gray color of the volume and surface. The gray zones were characterized by increased average size of grains and the highest density (2.99 – 3.00 g/cm³), which is close to the theoretical density for BeO (3.01 g/cm³). Petrographic studies with an optical microscope established that the gray zones in the ceramic have an average grain size of 40 – 50 μm , a maximum size of 55 – 65 μm , and a minimum size of 4 – 7 μm . The pore size in these samples varies within the range of 1 – 5 μm . The average size of microcrystals in white samples varies within the limit of 15 – 20 μm , the maximum size 24 – 30 μm , the minimum size 2 – 3 μm , and the pore size varies from 1 to 6 μm .

The earlier performed studies [3, 4] indicated that the color of ceramics is related to the presence of iron impurities

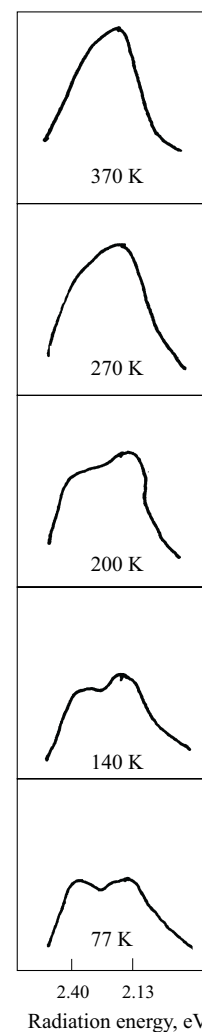


Fig. 1. Modification of the shape of PL peaks of beryllium ceramics depending on temperature.

(mostly in the form of Fe^{3+} ions), which presumably exist in the form of clusters of the type $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$ and $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{2+}$ located on the surface of BeO microcrystals. The mechanism of formation of this phase is not fully investigated. The impurity phase leads to substantial (1.5 – 3.5 times higher) recrystallization of BeO microcrystals, compared to the white-colored zones. The ceramics in the gray zones show increased light transmission in the visible and UV spectrum ranges.

The performed experiments established that PL of the dense gray-colored samples is 10 – 20 times more intense than that of the white samples. The PL spectra of the gray samples constitute complex peaks with maximum in the range of 3.49 eV. The PL maxima of the white ceramics (without impurities) are slightly shifted toward lower energy compared to the gray samples.

The PL curves in samples of different colors vary significantly in their half-width. The half-width of PL peaks of the tinted samples is about 2.5 times lower than that of the white samples.

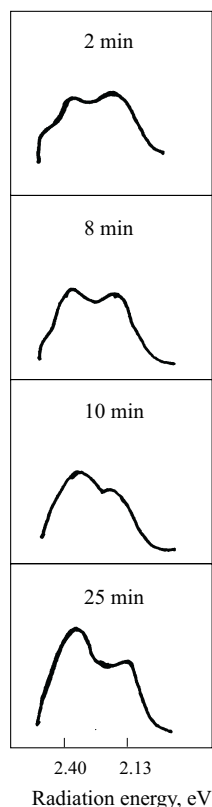


Fig. 2. Modification of the shape and intensity of PL peaks of beryllium ceramics depending on the duration of laser radiation at temperature 77 K.

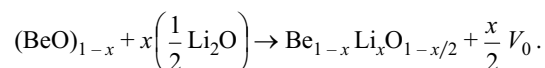
The PL spectra of BeO samples of density 2.90 g/cm^3 (without introduced impurities) excited at different temperature with a pulse argon laser (3.67 eV) are shown in Fig. 1. The PL spectral curve in the temperature interval of 300 – 370 K consists of one maximum: 2.21 eV. As the temperature drops to 77 K, the spectral curve is split into two maxima: 2.40 and 2.13 eV.

Of special interest is the modification of the shape of the PL spectral curve in the course of exposure of the samples to a laser beam at temperature 77 K (Fig. 2). At the initial moment, the intensity of both maxima (2.40 and 2.13 eV) was equal. As the duration of the sample exposure to laser radiation is prolonged (for 10 min and more), the intensity of the maxima became redistributed. The intensity of the PL peak 2.40 eV grew, whereas the intensity of the peak 2.13 eV, on the contrary, decreased. The PL intensity (peak 2.40 eV) was stabilized after the sample was exposed to laser radiation for 30 – 40 min. The intensity of the peak 2.13 eV became stabilized after the samples were radiated for 40 – 50 min.

The excitation of pure ceramic samples and samples with alkaline impurities employing a powerful excimer UV laser (6.42 eV) produced PL of one band with the maximum 3.35 – 3.49 eV (Table 1). A similar PL band (3.49 eV) was observed by the authors in [5] when exciting BeO single crystals in the absorption band with a radiation energy of 6.6 eV. The authors attributed the presence of this band to electron transitions in the F^+ center. The samples in that case were excited with a powerful krypton lamp. Using the

excimer laser (6.42 eV), we were able to excite PL in the same band. The shift of the PL maximum of the band depending on the concentration of impregnating alkaline solutions (i.e., on the quantity of the introduced alkaline metal impurity) toward lower energy values is presumably due to the effect of the impurity phase on the PL centers in beryllium ceramics.

The PL spectra of pure samples excited with an argon laser (3.67 eV) at temperature 300 K exhibited a PL band with a radiation energy of 2.21 eV. At temperature 77 K, this band was split into two clearly observed maximums with energy 2.13 and 2.40 eV. The band 2.13 eV, in our opinion, is also related to the F^+ center determined by the presence of impurities. With a low content of Li^+ and Na^+ ions (10^{-3} – 10^{-4} wt.%), they bring about heterovalent replacement of Be^{2+} ions in the cation sublattice [2]. The scheme of the formation of solid substitution solutions $\text{BeO} - \text{Li}_2\text{O}$ can be represented as follows:



As the result of replacing Be^{2+} ion with Li^+ ion, oxygen vacancies V_0 emerge, whose existence in the course of irradiation of the samples is accompanied by the formation of F^+ centers. The oxygen vacancies in BeO generated in this way have a great effect on the luminescence intensity and lead to its significant intensification [1, 2].

The results of heat treatment of samples in hydrogen is the formation of an additional quantity of anion vacancies, mostly on the surface of the microcrystals, which is typical of the initial stage of thermal reduction of BeO. This explains the significant increase in the intensity of PL of the samples calcined in hydrogen,

The impurities introduced into BeO as a second phase can enter in chemical reactions with BeO in the course of ceramic sintering and form new compounds, i.e., beryllates of alkaline metals [6], and can as well concentrate along the boundaries of microcrystals and pores, thus suppressing PL. As was shown in [6], the maxima of the luminescence spectra of alkali metal beryllates are shifted towards the violet range of the spectrum, compared to pure BeO. This can account for the shift of the maximum toward greater wavelengths and a significant decrease in PL intensity in the samples of beryllium ceramics impregnated in NaOH solution of the concentration 100 g/liter, which has the maximum content of sodium impurity.

The sodium and lithium impurities isomorphically incorporated in the crystalline lattice instead of Be^{2+} ions, on the contrary, increase the PL intensity of the samples due to the appearance of oxygen vacancies. The aggregation of impurities on the surface of BeO microcrystals is accompanied by screening of luminescence centers of BeO.

Sodium impurities on the surface of ceramics and microcrystals determine the formation of color centers, which significantly modify the shape of the PL peaks in the course of

exposure of the samples to the rays of an ultraviolet argon laser. The peak 2.13 eV, whose intensity becomes significantly weaker under laser radiation, is presumably related to the emergence of a color center or F^+ center.

Thus, beryllium ceramics in its pure form and with added alkali metals impurities exhibit photoluminescence when excited by ultraviolet laser radiation.

It is assumed that heat treatment of samples in hydrogen and introduction of lithium and sodium additives in small quantities produce additional PL centers localized in the impurity ions Li^+ and Na^+ , which increases the intensity of PL. In contrast, large concentrations of the impurity phase suppress PL. In heterovalent substitution of Li^+ or Na^+ ions for Be^{2+} , additional oxygen vacancies arise, in which under excitation electrons can be localized and F^+ centers can be formed.

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